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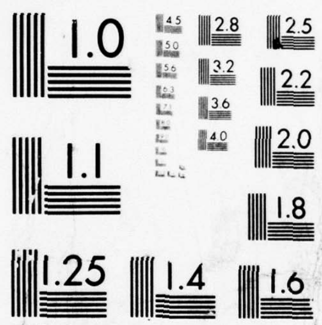

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Period Covered 1 October 1977 through 1 October 1978

(10) H. Lessoff

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Electronics Technology Division

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This report discusses the programs and progress made in the in-house portion of the Electronic Materials Program. The growth of semi-insulating III-V semiconductors using oxygen doping is discussed, including electrical and device characterization. Results of indium phosphide material preparation and bulk single crystals as well as epitaxial films growth are summarized. High magnetostrictive materials have initial permeability and coupling constants increased by nearly an order of magnitude.

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CONTENTS

Electronic Material Technology

(ZF54-581-001)

62762N Electronic Device Technology

In-House Laboratories' Activities FY-78

Period covered 1 October 1977 thru 1 October 1978

This report is a composite of summaries of the Navy's in-house laboratories' effort on the Electronic Material Technology Block for fiscal year 1978. The block's origins are based on the premise that functional electronic and electro-optic devices and systems are intimately dependent on the materials used in such systems and devices.

Program Manager: H. Lessoff, Code 5220
Naval Research Laboratory
Washington, DC 20375

Electronic Material Technology
(ZF54-581-001)
62762N Electronic Device Technology

Summary Report - 28 February 1979

Background:

A. The Electronic Material Technology (ZF54-581-001) is a DDF Block at NRL, Code 5220, established in FY'78 at a funding level of 1.126M and has a current funding level of 1.2M in FY'79. The Block in electronic materials has been developed in direct support of program needs in electronic and electro-optic devices and systems where new developments are often inhibited by the lack of adequate material technology.

Currently the Block is organized in material technology for two major thrusts:

o Microwave and millimeter wave solid state devices,

o Electro-optics, communications and control systems,

and complimentary thrusts:

o Improved microwave tube materials,

o Materials for laser applications,

o Signal processing materials.

The programs strive to insure the realization that electronics and electro-optic systems are not hindered by the lack of adequate material technology.

The current available electronic materials place limits on today's device technology and unless new materials are developed then further limitations will occur in projected devices and systems. The Block Program is organized to address and overcome

Note: Manuscript submitted March 16, 1979.

current and future material barriers in order to meet device and system needs.

<u>Objectives</u>: The objectives of this Block closely address the major identified material needs in the Electronic Devices and Electro-Optics Technology Exploratory Development Strategy. The needs are addressed in the following manner:

- o To determine those material problems which limit new devices and systems development.
- o To establish the material requirements.
- o To carry out the necessary development to overcome the material barriers.
- o To select from 6.1 activities those promising material development for transfer to 6.2 programs.
- o To develop the materials sufficiently for transfer to 6.2 and 6.3 programs and to manufacturing technology.

Among the electronic/electro-optic identified materials needs are for improved or new RF and EO solid state devices, vacuum tubes, cryogenic devices, acoustic devices and structure and protective components and coatings. The total number of needs far exceed the available resources therefore selective material thrust are developed which appear to offer the largest DoD impact for the invested dollar.

Investment consideration is made in areas where the electronic industry, because of limited commercial incentive, will not meet the military requirements.

Block Opportunities and Technical Issues:

In order to determine the proper investment course for the material progams, the electronic and electro-optic technology thrusts as projected in their current exploratory development are examined and those areas of material deficiency are identified. From the list of potential material needs and the potential of solution, the material program is developed. When feasible the material programs are selected such that two or more projected needs can be met with one material thrust.

The major effort in the III-V compound semiconductor is intimately related to three major devices and systems thrusts a) electro-optics; b) signal processing; and c) microwave and millimeter wave technology. Electro-optics require improved materials for solid state lasers, fibers, detectors and light emitting diodes. Signal processing requires functional electronics and integrated devices having speed capability beyond that available in a silicon based technology. The microwave and millimeter wave technology require solid state sources, amplifiers, monolithic integrated circuits, transmitters receivers, et cetera, which operate up to 240 giga Hertz. By matching these requirements to material potential, it is quite apparent that a major investment was and is required in III-V materials. The Material Block has programs directed towards preparing and understanding III-V bulk and epitaxial single crystals of GaAs, InP, as well as ternary and quaternary alloys. The program has successfully capitalized on very strong in-house capability at NRL and NOSC with associated activities in industries and universities. The Electro-Optics thrust will be transferred to a new program called Electro-Optics Material

Technology and will include work units in this program that are directed towards Electro-Optic Applications.

The growth of bulk single crystal InP and GaAs is a typical activity in this program. The single crystals are used as substrates for subsequent growth of epitaxial layers for detectors, lasers and light emitting diodes. The same single crystal materials are used for epitaxial growth or ion implantation of active areas for integrated logic and memory components as well as for microwave and millimeter wave devices. Of the technology based needs as described in the Electronics and Electro-Optics Strategy (Feb. 1978) this program directly relates to 3 of the 4 identified major activities.

Another thrust in military electronics is the continuing need for higher power, longer life microwave tubes. This need receives very limited support from industries and universities since the requirements are very unique to DoD activities. Although solid state technology is making inroads on applications of low power low noise tubes, especially the travelling wave tubes; the high power needs for surveillance cannot in the forseeable future be met by semiconductor devices. A program has been initiated attempting to make a cathode-grid structure which can be related to processing available in the semiconductor electronics industry yet meets the high power microwave needs. Included in this program is the development of dispenser cathodes which will operate at lower temperature than current cathodes and thus extend the operating life of a tube.

Acoustic devices and especially sonar has received very limited funds for material and/or new technology in the commercial sector. Of course beyond very limited commercial applications

the major user is the Navy for strategic applications. Current materials for active sonar devices are mainly ceramics especially lead zirconate titanate (PZT). The ceramics are brittle, have limited lifetimes, and cannot go to very low frequencies where the sound propagation in the water would be greater. There is a demonstrated need for very low frequency sonar devices which have improved performance over currently available piezoelectric materials such as PZT. Magnetic materials having very large magnetostrictive coefficients may be suitable for this application as well as use in other acoustic devices.

A program has been initiated to determine methods of achieving greater stability in chemical dye lasers. These materials have been proposed for use in airborne underseas surveillance; however, current dyes are not stable and decompose on use. Another program is being initiated in an attempt to produce solid state lasers based on rare earth fluorides which would result in a laser for operation from 0.6 to 5 μm. It is anticipated that the solid state laser system would have greater stability and decreased systems complexity when compared to a similar system based on the chemical dye laser.

A program has also been initiated in the growth of optical fibers having high resistance to radiation. Current fibers are quite susceptible to radiation and therefore systems based on optical fibers are quite vulnerable. NRL has developed some fiber compositions which have greater radiation hardness. These compositions are being prepared in industry along with attempts to develop matching coating glasses and thus enhance system survivability.

Omittedly many material programs have not been funded in this program such as magnetic material for microwave applications, ferri-electrics for acoustics and coating and potting materials. The funded activities were developed to achieve maximum impact on a variety of system and devices needs. When possible, material programs were undertaken in order to satisfy more than one major thrust area such as electro-optics and signal processing. In some cases the program attempted to fill an area where only the DoD or the Navy had specific needs which were not being addressed by the electronic industry such as the radiation resistant optical fibers, the magnetostrictive materials, or the long life, high power cathodes.

Achievements to Date FY'78/79:

(1) Semi-insulating gallium arsenide (GaAs) substrates have shown to be capable of direct ion implantation and to yield state-of-the-art Field Effect Transistors (FET). The process to make the material is being transferred to Manufacturing Technology and already four major electronic companies are picking up the developed technology. (NRL and Avantek)

(2) Semi-insulating iron doped indium phosphide (InP) has been grown with lower iron doping due to higher purity of the indium phosphide. Substantial benefits using this material are being noted in both electronic and electro-optic device technology. (NRL)

(3) The source of the manganese in the converted layer of heat treated GaAs substrates has been determined and methods to reduce conversion have been addressed. (NRL)

(4) Transient capacitance technique has been developed and automated to lead to routine identification of deep level impurities and defects in compound semiconductors. (NRL)

(5) The first successfully fabricated ion implanted InP FETs with x-band microwave performance have been prepared and demonstrated. (NRL)

(6) A qualification and encapsulation method has been developed for semi-insulating InP which when properly used shows no evidence of surface conversion or conduction. (NRL)

(7) The use of undoped semi-insulating GaAs as prepared at NRL has been demonstrated to be a major advance in preparing ion implanted FETs. (NRL)

(8) Thermal degradation of InP has been studied and a method based on phosphine gas overpressure developed to prevent degradation. (NOSC)

(9) Advances in metal insulator semiconductor field effect transistors (MISFET) have been made and devices have been made. (NOSC)

(10) The optical properties of InP over the spectral region of 1 eV to 15 eV have been made in conjunction with band structure of InGaAsP. These measurements are directly related to electro-optic sources and detector properties. (NOSC)

(11) A method has been developed and demonstrated which when using electro-reflectance is able to determine uniformity of carrier concentration across a III-V wafer. (Univ. of Illinois, Chicago Circle)

(12) A chloride system for the preparation of high purity

indium phosphide has been assembled and initial runs have been made. (Univ. of Washington, St. Louis, MO)

(13) Semi-insulating layers of chromium doped GaAlAs have been grown on n-GaAs and optical and interface properties determined. (Stanford Univ.)

(14) A study completed for the feasibility of ferrite materials use at millimeter wave frequencies. (NRL)

(15) A mechanism has been determined which indicated the primary degradation of zirconium non-bonded grids is due to barium retention. (NRL)

(16) Organic binders used in making alkaline earth oxide cathode coatings have shown to form an eutectic with barium carbonate which significantly reduces the cathode emission. (NRL-Varian)

(17) Permeability in the high magnetostrictive rare earth iron alloys has been improved an order to magnitude by orientation of crystallites during annealing and reduction of a second phase. (NSWC)

(18) Coupling factors of the rare earth iron alloys have been signficantly increased while maintaining a high strain level. (NSWC)

(19) Special glass melts for optical fibers have been prepared of compositions having higher radiation tolerance than current materials. (Owens-Illinois-NRL)

In the last year, the block has been responsible fully, or in part, for a number of publications and technical presentations. A partial listing is given in Appendix B.

Block Plans: This program will be split into two (2) separate but closely coordinated programs. This current one shall substantially have the microwave and millimeter wave materials activities. A new program shall be initiated called Electro-Optic Materials

Technology (ZF62-583-003) and as such will include those programs which relate directly to new and improved materials for optic applications.

Funding Profile:

	FY-78	FY-79	FY-80	FY-81	FY-82
ZF54-581-001	1.126	1.2	1.0	1.20	1.32
ZF62-583-003	-	-	.6	.80	.88

List of Current Activities in Block: (Appendix A lists contracts)

a. Compounding and bulk single crystal growth of III-V single crystals.

b. Epitaxial growth of III-V semiconductors including binary, ternary and quaternary.

c. Ion implantation of III-V materials.

d. Insulators on semiconductors.

e. Growth and evaluation of IV-VI semiconductor detectors.

f. Purification of organic metallic compounds for semiconductor materials.

g. Material and device characterization.

h. Dye laser material stability.

i. Magnetostrictive material development.

j. Rare earth fluoride laser materials.

k. Radiation tolerant optical fibers.

In-House Program Summaries:

A summary of the activities in the Navy laboratories on the Block Program is given in this section. Copies of reports and additional information can be obtained by contacting the principle investigators.

Semiconductor Material Growth

Principal Investigators: E. M. Swiggard and H. Lessoff (Code 5220)
Naval Research Laboratory, Washington, D. C. 20375

Emphasis during the last year has been directed at (a) improving the quality of semi-insulating GaAs substrates and (b) determining methods of reducing trapping states at the substrate-epitaxial layer interface. Attention was also directed at preparing semi-insulating InP substrates. The results obtained to date in this program are coordinated with a materials characterization program at NRL such that rapid feedback is available at each stage of material processing. The characterization feedback helps define needed areas for work to further improve the material preparation and growth.

The material program is a broad-based activity which considers that each processing parameter must be rigidly controlled from the initial elemental purity to the final device evaluation. Therefore, the current program was subdivided into the following tasks: (a) compound preparation; (b) bulk single crystal growth; and (c) substrate finishing and epitaxial growth. Each step in processing is evaluated with continuous feedback between the characterization effort and the material program. Samples of materials prepared were and are being submitted to various laboratories for characterization and use in device fabrication.

Compounding GaAs

Forty-nine ingots of GaAs have been compounded in PBN by the method previously described. Thirty-four of these ingots were semi-insulating 1" from the first end to freeze. Five of the ingots that were not semi-insulating were traced to a contaminated lot of arsenic. It has not been possible to determine why the other ten ingots were not semi-insulating. The non-semi-insulating ingots appear to be n-type but the Van der Pauw

measurements were so ambiguous that they could not be analyzed. The conductivity between the various contacts indicated a very inhomogeneous material. PBN compounded GaAs is very polycrystalline and it is not possible to select single crystal areas for electrical measurements.

It is evident that a clear picture of the impurity concentration cannot be found by looking at the electrical data on the polycrystalline ingots. A series of single crystals were pulled using semi-insulating charge material, conducting charge material and semi-insulating charge material with known Te additions.

GaAs Single Crystal Growth

It has been shown that undoped PBN-LEC GaAs can be produced consistently. The defect density in LEC crystals can be very good. Undoped PBN-LEC GaAs substrates are very promising for ion implantation and VPE when an in-situ etch of the substrate is used. A model indicating oxygen as the deep center which determines the S.I. character of the material has been proposed. Efforts to intentionally introduce oxygen will be attempted to increase the yield of S.I. GaAs in each crystal.

Considerable progress has been made toward obtaining a thermally stable S.I. substrate that is reproducible. Additional Cr-Te ratios are indicated. Also other dopants such as Sn will be investigated. This technology is scheduled for a Manufacturing Technology program in fiscal '79.

InP Growth and Compounding

An experimental procedure for synthesizing bulk InP has been developed to produce high purity charge material for LEC crystal growth. The procedure described in this report produces InP charge material with N_d-N_a at mid $10^{15}/cm^3$ and with 77K mobility values as high as 45,700 cm^2/vs. The charge material

has been doped with Fe to grow semi-insulating LEC InP crystals and the effective segregation coefficient of Fe in InP has been determined to be 1.6×10^{-3}. Knowledge of the segregation coefficient along with the availability of the high purity charge material has permitted the Fe concentration in the LEC crystals to be lowered to approximately $10^{16}/cm^3$ and still consistently produce semi-insulating InP. The procedure used for the LEC growth of InP has reduced but has not eliminated the incidence of twinning. The problem of twinning needs further understanding in order to increase the availability of InP substrates.

Liquid Phase Epitaxial GaAs Growth

Procedures for the liquid phase epitaxial (LPE) growth of GaAs layers suitable for Field Effect Transistors (FET) have been defined. The procedure uses a pregrowth gallium etch to dissolve a layer of the substrate surface immediately prior to epi layer growth; the resulting reduction of surface irregularities and surface states caused by thermal damage during the heating cycle minimizes or eliminates the need for a buffer layer.

Pregrowth substrate cleaning procedures have been defined and the effect of growth variables explored. Cusp formation in the grown LPE layer, for example, can be minimized by precise on-axis (100) substrate orientation and by using a well-established cooling ramp to achieve uniform growth conditions in the LPE Ga-etch procedure.

Tin was used as a dopant to grow n-type GaAs LPE layers suitable for FET manufacture (2000-3000Å thick, $n \sim 1 \times 10^{17}/cm^3$). Tin distribution coefficients were determined and were found to be consistent with literature values; they are apparently unaffected by the pregrowth gallium etch.

Evaluations of FETs made by a commercial laboratory on NRL produced material (NRL substrates and NRL Ga-etch LPE) are

encouraging: for equivalent noise figures higher gains are obtained on the NRL material as compared to VPE, non-etch LPE, and ion-implanted material.

Characterization of Electronic Device Materials

Principal Investigator: B. D. McCombe, (Code 5270)

Naval Research Laboratory, Washington, D. C. 20375

During the past year the characterization effort has concentrated on four main tasks. 1) Further effort directed at understanding the details of the compensation mechanism producing the NRL not intentionally doped semi-insulating GaAs and the p-type ends of ingots. 2) Definitive identification of the "Defect" causing type conversion in heat treated GaAs. 3) A coordinated growth, characterization and device fabrication-evaluation study of LPE active GaAs layers on bulk Semi-Insulating substrates, and 4) Characterization of Bulk InP. In addition, further development work on techniques was carried out. This includes the completion of a computer automated, temperature scanned Hall effect apparatus, and the computerization of the deep level transient capacitance apparatus with digital data acquisition, analysis and computer control of the temperature scan. The latter development permits a 30-fold improvement in data acquisition time and holds the promise of making the transient capacitance technique a routine tool for identification of deep level impurities and defects in compound semiconductors.

Task 1

Photoluminescence and Hall measurements coordinated with extensive doping studies, Hall measurements and SIMs measurements at Thomson CSF in France, have led to the following tentative conclusions: a) The semi-insulating behavior in the NRL not intentionally doped bulk GaAs is a result of the dominance in these relatively pure materials of a deep level donor defect which may be related to the presence of oxygen; b) the conversion of approximately one third (the melt end) of many of the recently

grown ingots to conducting p-type is due to the accidental introduction of a shallower acceptor-like impurity or defect with an activation energy of 0.15 eV obtained from temperature scanned Hall measurements. A tentative identification (from the activation energy) of this acceptor as copper is not conclusive since the characteristic copper photoluminescence band was not observed in these samples. The possibility that an intrinsic acceptor-like growth defect is responsible cannot be ruled out.

Task 2

A series of coordinated studies of bulk Mn-doped GaAs samples obtained from Hewlett-Packard were carried out. Measurements included temperature scanned Hall effect, photoluminescence, mass spectroscopy (by Hewlett-Packard), and electron spin resonance (by NRL Code 5290). Results demonstrate conclusively that Mn occupies Ga sites, acts as an acceptor with an activation energy of approximately 0.1 eV, and exhibits a characteristic photoluminescence band peaked at 1.41 eV identical to that seen in heat treated bulk GaAs. Thus we conclude that the type-conversion observed in bulk GaAs heat treated in the usual pre-LPE growth cycle under Hydrogen is directly related to Mn impurities. Further efforts are in progress to determine the source of the Mn and the manner of its introduction into the thin surface layer. Preliminary indications are that the source is the heated Pd diffuser in the Hydrogen purifiers. This work was performed in cooperation with the material growth program (NRL Code 5220).

Task 3

During the past year an extensive program was undertaken in an attempt to correlate materials and processing characteristics with final device performance (Schottky Barrier Field Effect Transistors) for carefully controlled LPE active layers grown

on selected semi-insulating GaAs substrates. Substrates from three different sources were used: NRL undoped material; NRL Cr:Te doped material, and Laser Diodes Cr-doped material. Liquid Phase Epitaxial layers were grown on pairs of these substrates, one with a pre-growth Ga etch and one without. Each of the resulting wafers was subjected to an extensive series of characterization studies including photoluminescence, Hall effect and microwave conductivity, measurements, C-V profiling, and deep level transient capacitance spectroscopy; as part of this effort ohmic and Schottky contacts were fabricated by Code 5210 for the Hall, C-V, and DLTS measurements. Wafers were also processed into devices and evaluated by NRL Code 5210. Due to difficulties in processing into narrow gate devices apparently related to surface morphology, all of the goals of the effort could not be met. However, a number of useful results were obtained:

a) Low temperature photoluminescence measurements reveal the presence of shallow and deep impurities and defects in the active layer, the substrate and their interface. A characteristic interface PL band due to Mn was observed in all samples that were not subjected to a pre-growth Ga etch, and by induction the presence of a p-type layer at the interface.

b) Obvious rejection criteria for the active layers can be obtained from the C-V profiles, e.g., layer too thick, doping density wrong, etc.; however, it was not possible to correlate anomalies in C-V profiles with device noise, etc., as originally intended due to the aforementioned processing problems.

c) C-V and van der Pauw Hall determinations of carrier density were generally in good agreement. Both methods are useful particularly in combination, since the C-V measurements yield the electrical thickness and a profile of the active impurity concentrated while the Hall measurements measure the product of the average carrier density and the thickness of the conducting layer.

Task 4

Deep and shallow electron traps have been observed in NRL bulk undoped InP from transient capacitance measurements on MOS structures. The deeper of these traps may be due to residual Fe impurities which are also observed in these samples in photoluminescence measurements. Optical absorption measurements of InP:Fe have been shown to be capable of determining the concentration of Fe^{2+} (compensated Fe) impurities semi-quantitatively.

GaAs FET Device Fabrication and Ion Implantation Technology

Principal Investigators: Dr. Kenneth J. Sleger
Dr. Harry B. Dietrich
Code 5210, Naval Research Laboratory, Washington, D. C. 20375

Microwave Schottky barrier FETs and ion implantation have been selected to provide a benchmark technology for evaluation of III-V compound semiconductor materials grown at NRL and elsewhere. FETs used here employ a nominal one micron gate length and are processed by a combination of conventional contact photolithography and liftoff techniques.

Ion implantation studies have centered about creating doping profiles suitable for active layers in GaAs and InP FETs using semi-insulating (SI) substrates. These substrates are previously qualified by capping with plasma deposited Si_3N_4 and annealing between $800^{\circ}C$ and $850^{\circ}C$ for 15-30 minutes (GaAs) or $700^{\circ}C$-$750^{\circ}C$ for 15 minutes (InP). Samples which show surface conversion after the anneal are rejected. NRL has demonstrated proficiency in being able to implant, cap and anneal both GaAs and InP SI substrates.

GaAs FETs were fabricated on ion implanted NRL SI substrates (unintentionally doped) and on commercially supplied Cr doped SI GaAs with epitaxial channel regions. At 10 GHz the noise figure ranged from 3.4 dB - 3.8 dB with 6-8 dB associated gain for these devices. Differences in microwave performance between ion implanted and epitaxial FET were correlated to differences in mobility and velocity profiles obtained from fat FET test structures and actual microwave FET devices, respectively. Results suggest the need for improvement in FET process technology and capping technology.

High Work Function Materials for Microwave Tubes

Principal Investigator: Dr. R. F. Greene (Code 5230)

Naval Research Laboratory, Washington, D. C. 20375

The NAVMAT DDF Material Block has, following the recommendations of OUSDR&E, carried out a program in-house and on commercial contract for the improvement of cathode materials for microwave and millimeterwave tubes. The in-house program has established the suitability of Zr integral control microgrids by a study of the factors affecting stability of high work function Zr structures in contact with hot cathodes by measn of simultaneous work function, Auger, temperature, and other measurements. The details of these measurements and recommendations for future grid programs have been prepared for publication in the open literature (Annual Report, enclosure (1)). Having completed this effort, the in-house work has been redirected to the preparation and characterization of preferred orientation iridium, tungsten, and osmium foil substrates for controlled porosity dispenser cathodes. This was motivated by the earlier in-house observation that certain crystal orientations support oxide films with almost an order of magnitude enhanced thermionic emission compared with random orientations, and by the possibility of using CVD and other techniques for production of preferred orientation metal surfaces. A new technique, microspot LEED, is being prepared to determine the orientation of microcrystals too small for conventional X-ray identification. Selected area channeling methods will also be utilized for orientation where applicable.

The contract program, carried out at Varian Associates, has carried the controlled porosity dispenser (CPD) concept, developed at NRL, into the fabrication of actual concave cathodes, incorporation into commercial TWTs, and emission testing under realistic conditions. Iridium foils were grown by sputtering and by electrodeposition onto molybdenum foil hole arrays (25 microns on 50 micron centers) photolithographically. Cathode emission density, operating temperature, poisoning resistance, and emission stability were shown to be several times better than all previous commercial cathodes. Further effort is being expended to prepare materials for an integral grid and improving emission density.

InP Growth and Evaluation

Principal Investigator: H. H. Wieder

Naval Ocean System Center, San Diego, CA 92152

Introduction

The work described in this summary was performed under NOSC Program EE 03 and funded through NRL from NAVMAT funding for III-V semiconductor material research. The objective of this program is to develop simple, reliable, low cost methods of growing indium phosphide and III-V alloy epitaxial layers and to evaluate their metallurgical, electronic, and optical properties aimed toward their use for transferred electron device applications, field-effect transistor (FET) microwave logic circuits, time division multiplex communications systems and optoelectronic emitters and detectors.

InP Epilayer Growth

Investigation of liquid phase epitaxial (LPE) growth of InP and InGaAsP epilayers has addressed problems intrinsic to the use of In-P solutions and InP substrates. Thermal degradation of polished InP surfaces under conditions typical of LPE-growth was studied and a partial pressure of phosphine gas (PH_3) in the ambient hydrogen was utilized to prevent the degradation. The thermal degradation of InP results in phosphorous disassociation and formation of In-filled etch pits on the surface. Photoluminescence and electrical measurements of InP show no surface "conversion" effects characteristic of thermally-treated GaAs, even though the surface has been badly roughened by heating. Semi-insulating Fe-doped InP surfaces heated in hydrogen with a phosphine partial pressure above a threshold value related to the In-P-Ph_3 liquid-gas equilibrium show no roughening or electrical modification. A liquid phase epitaxial growth technique utilizing phosphine has produced InP and InGaAsP lattice-matched layers with very flat, well-behaved interfaces.

A technique of saturating the In-growth solution with phosphine concentrations of $\sim$750 ppm in the hydrogen ambient at temperatures from 650-700°C has been used. This is an effective technique but it has revealed dramatically the importance of considering all the vapor interactions with the solution and substrate in determining epilayer quality. The use of hydrogen and phosphine with less than 1 ppm H_2O in the ambient gas results in severe transport of silicon to the growth solution with a commensurate increase in background donor concentration in the epilayers. The silicon concentration has been great enough in some cases to form a solid precipitate on the growth solution which is not InP (possibly SiP_2). The silicon transport can be prevented, and even reversed by introduction of 10^2 to 10^4 ppm H_2O into the ambient gas during solution saturation. InP epilayers with carrier concentrations of $<10^{16}$ cm^{-3} and 77°K electron mobilities of 20,000 cm^2/V-s are readily obtained from such growth solutions; however, the optimum use of H_2O has yet to be determined.

Various LPE growth conditions have been studied to achieve uniform thickness submicron epilayers suitable for FET fabrication. Generally, the InP epilayer thickness uniformity is limited by a low density of nucleation sites which grow 3-dimensionally to give an uneven surface topography. For layer thickness of 0.2-0.3 μm the surface height variations are frequently equal to the thickness. The nuclei shapes and distribution are very sensitive to substrate orientation and seem to correlate to the orientation dependence described by other investigators. Two different growth systems have been used for the submicron InP growth; one used the PH_3 for saturation and prevention of substrate degradation; the other used dry hydrogen and a separate In etch-melt to remove surface damage and contamination from the substrate before layer deposition. Nucleation characteristics of layers from the two systems were similar. To achieve a higher

nucleation density, growth has been initiated from supercooled solutions, typically from 7 to $15^{o}C$ below a liquidus of $680^{o}C$. While this has aided in growth of some layers unsuitable for FETs, the results are not consistently smooth. Evidence reveals an additional nucleation mechanism related to meniscus lines associated with the edge of the supersaturate solution moving onto the substrate surface. The surface features have become a series of closely-spaced ridges perpendicular to the motion of the substrate under the solution independent of orientation. These ridges limit the layer smoothness by the same magnitude as the thickness necessary for FETs with some exceptions. The occasional smooth layer stimulates the search for a causal relationhip to the substrate orientation and the condition of the growth solution. In the meantime the thickness non-uniformity of LPE InP submicron epilayers is a serious limitation to device technology.

Materials Characterization

Investigations of the properties of the surfaces and interfaces of InP and related III-V semiconductors have been a major part of the characterization efforts of this program in conjunction with related MISFET investigations at NOSC. Experimental measurements made on InP and InSb MIS structures have been interpreted in the context of the experimental and theoretical framework developed for the $Si-SiO_x$ MOS system. GaAs and InAs MIS structures exhibit anomalies attributed principally to pinning of the Fermi level by extrinsic surface states near midgap for GaAs and within the conduction band for InAs. Microwave power gain can be obtained from InP and GaAs MIS FETs irrespective of the density of fast surface states present in them. The surface states cannot respond to the μ-wave signals applied to the MISFET gates.

Optical constants of InP have been measured over the spectral region 1 eV to 15 eV in conjunction with bandstructure studies of InGaAsP. Room temperature reflectance data from (001)-oriented InP have been analyzed with Kramers-Kronig relationships to determine the optical properties. This method is particularly suited for investigating optical properties of materials in the region corresponding to quantum energies where absorption coefficients rise above 10^4-10^5 cm^{-1} making transmission measurements difficult. Values of index of refracion and optical absorption have been determined for the spectral range 0.18 to 2 μm.

Details of InP characterization investigations, and related work on MISFET devices have been thoroughly reported in the open literature and in NOSC Technical Notes available from the authors.

Magnetostrictive Rare-Earth Transistors Metal Alloys

Principal Investigator: A. E. Clark

Naval Surface Weapons Center, Dahlgren, VA 22448

The magnetic and magnetomechanical material properties study is part of a program to develop magnetostrictive materials for high power sonar projectors. The rare earth iron Laves phase compounds containing terbium possess high magnetostrictions and when they are prepared in textured form become excellent candidates for driving elements of high strain transducers.

Grain-oriented samples of highly magnetostrictive rare earth-iron compounds have successfully been prepared. These samples possess lower inhomogeneous strains than found in the random polycrystalline RFe_2 compounds, resulting in much higher values of relative permeability (μ_r) and magnetomechanical coupling (k_{33}). A partially oriented $Tb_{.20}Dy_{.22}Ho_{.58}Fe_{1.95}$ sample was prepared using a pyrolytic Bridgman type boron nitride crucible. At a bias field of 100 Oe $k_{33} = .73$, which is considerably larger than found in the random polycrystal of the same composition. A relative permeability of 36 occurs in this same sample when a low ac drive of 1.6 Oe rms is used. A second fabrication method using a horizontal zone technique with a supporting "cold finger" was employed to grow the ternary $Tb_{.27}Dy_{.73}Fe_{1.98}$. The low ac drive values of k_{33} and μ_r were .74 and 19 respectively. The permeability at low bias was found to possess a sharp ac drive dependence. Near zero bias, when the drive was changed from 1.6 Oe rms to 13 Oe rms, μ_r in the quaternary increased from 36 to 98. In the ternary the values of μ_r near zero bias increased from 19 to 61. Magnetostriction measurements on both samples show a significant increase in $d\lambda/dH$ and λ_s over the random polycrystals.

Appendix A

Contract Activities

1. N00173-78-C-0242. Radiation Resistant Glasses, Owens, Illinois, Toledo, Ohio. Dr. L. V. Pfaender
2. N00014-78-C-0297. Preparation and Properties of $Al_xGa_{1-x}As:Cr$, Stanford Univ., Stanford, CA. Prof. T. L. Pearson
3. N00173-78-C-0195. High Purity GaAs by Metalorganic CVD, Rockwell International, Anaheim, CA. Dr. H. M. Manasevit
4. N00173-78-C-0129. Shallow Donor Impurities in High Purity Semiconductors, Univ. of Illinois, Urbana, IL. Prof. G. E. Stillman
5. N00173-78-C-0437. Topographic Examination of Semiconductor Systems, Univ. of Illinois, Chicago Circle, Chicago, IL. Prof. S. Sundaram
6. N00173-78-C-0431. High Purity Epitaxial InP, Washington University, St. Louis, MO. Prof. C. M. Wolfe
7. N00173-78-C-0214. FET Evaluation Study, Avantek, Inc., Santa Clara, CA. Dr. M. Omori

Appendix B

Publications and Presentations

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